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Author(s)	Hasanudin; Kuroda, Noritaka; Sugimoto, Toyonari; Mogi, Iwao; Watanabe, Kazuo
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High-pressure infrared absorption in Cs₂TCNQ₃ crystals grown under magnetic field

Hasanudin^{1,2}, N. Kuroda^{2,3}, T. Sugimoto⁴, I. Mogi⁵, K. Watanabe⁵

¹*Faculty of Engineering, Tanjungpura University, Pontianak 78124, Indonesia*

²*Department of Mechanical Engineering and Materials Science,*

Faculty of Engineering Kumamoto University, Kumamoto 860-0855, Japan

³*CREST, Japan Science and Technology Corporation, Kawaguchi 332-0012, Japan*

⁴*Research Institute for Advanced Science and Technology,*

Osaka Prefecture University, Sakai 599-8570, Japan

⁵*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

Abstract

Pressure dependence of infrared absorption has been measured in Cs₂TCNQ₃ single crystals grown under magnetic field of 5 T (5 T crystals). The behavior of the C-CN as well as C-H stretching modes suggest that there occurs a phase transition which resembles to the one related to the insulator to metal transition in the crystals grown without magnetic field (0 T crystals). This transition, however, takes place at 4.1 GPa, slightly higher than the case of 0 T crystals. The charge transfer degree of the neutral and radical molecules are found to be $\rho = 0.30$ - 0.37 and 0.81 - 0.85 , respectively, which are significantly different from that of 0 T crystals. These differences are suggested to arise from the changes in the relative positions of the TCNQ molecules, as indicated from the behavior of the EMV mode.

Corresponding author:

Dr. Hasanudin

Department of Mechanical Engineering and Materials Science,

Faculty of Engineering, Kumamoto University,

2-39-1 Kurokami Kumamoto 860-8555

Phone: 096-344-2111 ext. 3704

Facsimile: 096-342-3710

e-mail: hasan@msre.kumamoto-u.ac.jp

1. Introduction

The crystals of the organic semiconductor Cs_2TCNQ_3 have been successfully grown under the influence of magnetic field and remarkable changes in their optical, electrical, and magnetic properties compared to the crystals grown without magnetic field have been observed[1]. The optical absorption measurement results have shown that the absorption band arises from the inter-radical charge transfer transition remarkably intensified in the crystals grown under 5 T (hereafter will be denoted as 5 T crystals). Similar intensification is also observed in several electron-molecular-vibration (EMV) coupled infrared absorption bands. The temperature dependence of electrical conductivity shows that the crystals grown under 0 T (hereafter will be denoted as 0 T crystals) exhibit two different activation energies, indicating that acceptors dominate the carriers below 290 K and the conductivity enters the intrinsic regime at higher temperatures. In contrast, 5 T crystals exhibit a single activation energy and acceptors dominate the carriers at all temperature region, suggesting that the number of acceptors is significantly enhanced in these crystals. In the point of view of magnetic properties, the remarkable change is observed in the temperature dependence of the magnetization. The ferromagnetic component of the magnetization collapses at around 300 K in 0 T crystals whereas it preserves up to 400 K in 5 T crystals. It is note worthy that the crystals of this substance have been grown under various magnetic field strength, and their optical properties suggest that they tend to exhibit the above-mentioned behavior if the applied field is higher than the threshold of 5 T.

These remarkable effects can be expected to arise from the changes in the crystals structure. Nevertheless, the X-ray diffraction analyses on the obtained crystals, within the experimental error, show no significant change in their crystal structure. The lattice constants, for example, remain unchanged. Those effects, therefore, must arise from microscopic origins.

We have previously measured the pressure dependence of optical absorption in the spectral region from near infrared to visible, to explore further details. It emerges from this measurement that the pressure dependence of the intensity of inter-radical charge transfer transition band S1 shows significant differences compared to that of the crystals grown without magnetic field[2]. These results suggest that some new electronic states have been created in the crystals grown under magnetic field. The details about the changes in the electronic structure, however, remain unclear. In the present work, further details of the electronic structure will be explored by means of high-pressure infrared absorption spectroscopy.

The present substance is an organic semiconductor, which is well known as the prototype of a 2:3 TCNQ compounds. It crystallizes in a monoclinic structure in which the donor Cs atoms and TCNQ molecules form segregated columns along the *b*-axis[3]. It is very well known that in this substance the excess electrons, i.e., the π^* electrons, provided by two Cs atoms are not uniformly distributed over the TCNQ molecules, but are localized on the certain molecular sites forming

TCNQ⁻[4]. The TCNQ molecular columns, therefore, are formed by the repetitive stack of the TCNQ⁻/TCNQ⁻/ TCNQ⁰ triads, where TCNQ⁰ and TCNQ⁻ are the neutral and radical TCNQ molecules, respectively. The Coulomb repulsion energy that causes this localization, $U \sim 1.2$ eV, is much higher than the transfer integral of ~ 0.1 eV[5]. Because of this localization, the electrical conductivity of this substance is not so high, only slightly higher than the insulating 1:1 TCNQ compounds. Its temperature dependence is a typical of *p*-type semiconductor, where deep level impurities play important roles particularly at low temperature[6]. In addition, interestingly, a ferromagnetism with small magnetic moment is observed in this substance, and this ferromagnetism remains even at room temperature[7]. The origin of this ferromagnetism, however, remains unknown to the date.

A pressure-induced electronic transition which resembles to the insulator-metal transition has been observed from the electrical resistivity measurement in the present substance[8]. This metal-like state, however, is considered different from that of ordinary metals, since no Drude tail is observed in the high-pressure phase[9]. High-pressure Raman scattering as well as infrared absorption studies have shown that π^* electrons of the TCNQ⁻ are significantly delocalized in the high-pressure phase[10,11]. The delocalization, however, is not complete so that the above-mentioned localization character is maintained, and therefore the substance maintains its semiconducting character. In addition, the infrared absorption data have also suggested that this phase transition is accompanied by a symmetry change in the relative position of the TCNQ⁻ radical molecules. In the low-pressure phase they are displaced against each other along the short molecular axis forming slipped dimers, and in the high-pressure phase those dimers turn into eclipsed ones[12].

Vibrational studies such as infrared and Raman spectroscopies have been proven as useful tools to study the electronic structure of a substance. Compared to other methods such as X-ray diffraction, these methods are technically easier, particularly for measurement under certain variables such as temperature or pressure. They give accurate information about electronic distribution on donors and acceptors of the charge transfer complexes[13,14], and therefore has been widely used to study insulator to metal[10] or neutral-ionic transitions[15]. In addition, those spectroscopies also give quite accurate information on the crystals structure. The situation of the dimer-monomer transition in the spin-Pierls system K-TCNQ and Rb-TCNQ[16], as well as the slipped-eclipsed dimer transition in (NMe₄)₂TCNQ₃[17], for example, can be revealed very well by infrared spectroscopy. Our previous work on the insulator to metal transition in the present substance explained above has also demonstrated that both information on the electronic distribution and crystal structure can be obtained at the same time by this method[12]. Furthermore, as mentioned previously, the effect of magnetic field cannot be detected by X-ray diffraction, but very well observed by infrared spectroscopy[1]. It is therefore, reasonable to employ this spectroscopy for further exploration on the properties the crystals grown under magnetic field.

The purpose of the present work is to explore further details about the differences in the properties of the crystals grown with and without magnetic field, in order to determine the new electronic structure induced by the applied field during the crystal growth. Considering the above-mentioned usefulness of the infrared spectroscopy, as well as the pressure-induced phase transition in 0 T crystals, we have measured the pressure dependence of the infrared absorption due to the molecular vibration in the 5 T crystals. The 5 T crystals are chosen as the samples because 5 T is the threshold field where the magnetic field effects appear. In addition the magnetic field effects in the 5 T crystals have already been characterized by several methods as explained above. We have particularly paid attention on the pressure dependence of the charge distribution over the TCNQ molecules, to explore the differences in the electronic properties of the crystals grown with and without magnetic field. The results will be discussed particularly within the framework of the above-mentioned phase transition.

2. Experimental procedure

The crystals are grown with the mix-solvent method under the magnetic field of 5 T. The temperature is regulated at 20° C. The details of this method have been previously explained[1]. The as grown single crystals, about 100x150 μm^2 wide, and 10 μm thick, are used as the samples. The wide surfaces of the samples are parallel to the *ab* plane of the crystals, and the probe light incident normal to these surfaces. The pressure is generated using a diamond anvil cell (DAC). Daphne oil and flourinert are complementarily employed as the pressure-transmitting medium, depending on the spectral region being observed, due to the problem explained previously[12]. The infrared absorption is measured using an FT-IR spectrometer equipped with a microscope. The ruby fluorescence method is used for calibrating the pressure.

3. Results

Figure 1 (a) and (b) show the unpolarized infrared absorption in the C-CN stretching region in 5 T and 0 T crystals, respectively, at several pressures. Figure 1 (b) is taken from ref. 12 for comparison. The thickness of the samples is $\sim 10 \mu\text{m}$. The features observed at 1205 and 1211 cm^{-1} at the ambient pressure are the infrared active $b_{2u}(\nu_{36})$ modes belonging to the neutral and radical molecules, respectively, whereas the one at 1184 cm^{-1} is the electron-molecular vibration (EMV) coupled mode[11,12]. The detail properties of the latter in several substances have been discussed elsewhere[18]. At low pressures, the two $b_{2u}(\nu_{36})$ modes behaves similarly in 0 T and 5 T crystals; they exhibit a blue-shift with increasing pressure, while increasing their frequency spacing. In 0 T crystals, at around 3.6 GPa they abruptly shorten their frequency spacing to appear like a broad single line. Above 3.6 GPa they keep blue-shifting without changing their frequency spacing. Similar behavior is observed in 5 T crystals as well, but the frequency spacing gets shortened at higher

pressure than that in 0 T crystals. Figure 1 (a) clearly shows a splitting of the $b_{2u}(v_{36})$ modes belonging to the neutral and radical molecules at 4.0 GPa in 5 T crystals, which is in contrast to that in 0 T crystals where they already appear as a broad single line at about the same pressure. The difference can be observed more clearly from the pressure dependence of frequencies of those vibration modes shown in Fig. 2. It is clear from the figure that the behavior of the both crystals, is very similar in the low-pressures but is different at high-pressures.

Significant differences can also be observed from the behavior of the EMV coupled mode observed at 1184 cm^{-1} . As clearly seen in Fig. 1 (a) and (b), the most distinct difference lies on the fact that EMV mode remains observable at pressures higher than 3.6 GPa, in contrast to the 0 T crystals in which the EMV coupled mode disappears. If we compare the spectrum at 4 GPa in both crystals we can clearly notice that in 5 T crystals the EMV coupled mode remains, whereas it is already disappear at the same pressure in 0 T crystals. The pressure dependence of the intensity of EMV band in both crystals displayed in Fig. 3. shows the difference more clearly. The EMV mode in 0 T crystals gradually intensified with increasing pressure up to 3.0 GPa, and abruptly diminishes at higher pressure 3.6 GPa. In 5 T crystals, on the other hand, the same band is gradually intensified as pressure increases up to 2 GPa, and abruptly decreases in some steps, to be barely observable at pressures higher than 5.5 GPa. This behavior is very similar to the pressure dependence of S1 band, the coupling counterpart of the EMV modes[2]. The pressure dependence of the frequency of the above-mentioned EMV mode in 5 T crystals is plotted together with that of 0 T crystals, and is shown in Fig. 4. It emerges from the figure that the EMV mode in the high-pressure phase of the 5 T crystals exhibits a red-shift with increasing pressure.

Figure 5 (a) and (b) show the infrared absorption spectrum in the C-H stretching region at several pressures in 5 T and 0 T crystals, respectively. The two modes appear at 3038 and 3054 cm^{-1} at ambient pressure are the b modes belonging to the neutral and radical molecules, respectively. The pressure dependence of these modes in both crystals are shown in Fig. 6. In both crystals at low pressures they are blue-shifted with increasing pressure while gradually reducing their frequency spacing. In 0 T crystals at ~ 3.0 GPa these modes shift toward lower frequencies while abruptly reducing their frequency spacing. They recover blue-shifting while maintaining their frequency spacing at pressure higher than 3.6 GPa. In 5 T crystals those mode tend to exhibit similar behavior, where they start to shift toward lower frequencies while reducing their frequency spacing at 4.1 GPa. The observation at pressures higher than 5.5 GPa, however, is difficult, since the C-H vibration modes become barely observable for the unclear reasons.

4. Discussion

The experimental results described in the preceding section clearly show the significant differences in the high-pressure properties of the crystals grown with and without magnetic field.

The behavior of the C-CN as well as the C-H stretching indicates that phase transitions with properties similar to each other take place in both crystals. In 0 T crystals this phase transition has been shown to be strongly related to an insulator-metal transition[11,12], whereas this particular relation yet to be studied in 5 T crystals. The major difference lies on the fact that this phase transition in 5 T crystals takes place at around 4.2 GPa, whereas in 0 T crystals this transition takes place at 3.6 GPa.

The properties of this phase transition that occurs at in 0 T crystals have been discussed previously. In general, the phase transition observed at 4.2 GPa in 5 T crystals is very similar to this transition, except that it takes place at higher pressure. The delocalization of π^* electrons seems to take place in 5 T crystals as well, as indicated by the abrupt decreasing of the frequency spacing between the vibration modes belonging to neutral and radical, particularly of the C-H stretching modes. The delocalization, however, is not high. The degree of the charge transfer estimated from the frequency of the C-H stretching modes at 5.3 GPa are $\rho = 0.30-0.37$ and $0.81-0.85$ for neutral and radical molecules, respectively. These values are significantly different from that of 0 T crystals, which give the values of $\rho = 0.46-0.50$ and $0.75-0.77$, respectively[12].

The EMV modes are originally forbidden in $E//a$ polarization, where E and a are the electric field of light and a -axis of the monoclinic crystal structure. They normally appear in the $E//b$ polarization, the stacking axis of the TCNQ molecules. In the present substance, however, they are also observable in $E//a$ polarization. This is because the TCNQ^- molecules are stacked in a way that they are displaced against each other along the short molecular axis, i.e. a -axis, to form slipped dimers[3]. Because of this slip, the dipole moment of the inter-radical electronic transition is not perfectly parallel to b axis, but is slightly canted and has a small component along a axis. This component couples with the molecular vibration to drive the EMV modes, which appear along the $E//a$ polarization with much smaller intensity compared to the modes appear in $E//b$ polarization. We have previously observed in the case of $(\text{NMe}_4)_2\text{TCNQ}_3$, which crystal structure is very similar to the present substance, that these modes disappear when the TCNQ^- dimers are no longer slipped due to the phase transition[17,19]. The intensity of the EMV modes appear in $E//a$ polarization, therefore, represents the amount of slip distance of the TCNQ^- dimers.

We have previously shown that the EMV modes observed in the unpolarized spectrum in this substance reflects the properties of that observed in the $E//a$ polarization of the linearly polarized spectrum[12]. We have, therefore, suggested that the disappearance of this mode in the high-pressure phase of 0 T crystals is as the result of the change in relative position of the TCNQ molecules, and the slipped TCNQ^- dimers turn into perfectly eclipsed ones, similar to the case of $(\text{NMe}_4)_2\text{TCNQ}_3$ mentioned above. The differences in the behavior of EMV band in respective crystals suggest that the relative positions of the TCNQ molecules in 5 T crystals might have been changed by the field. The changes, however, seem to be too microscopic to be detectable by the X-ray diffraction.

The temperature dependence of electrical conductivity in 0 T crystals has shown that there exists significant amount of acceptors, which dominate the conduction at low temperatures[1,6]. These acceptors, however, do not arise from the ordinary origins. The optical absorption spectrum in the mid-infrared region has shown that those impurities are associated within the columns of the TCNQ molecules[20]. We have suggested that these impurities arise from the disorder in the molecular arrangement of the TCNQ molecules along their columns. The concentration of these impurities increases in the crystals grown under magnetic field[1], which can be interpreted as the increasing of those disorders. This is actually one of the expectable effects of growing the present substance under magnetic field. It has been previously mentioned in the beginning, that in the crystal structure, there exists neutral TCNQ molecules, and charged TCNQ⁻ molecules and Cs⁺ ions. The crystals of this substance are grown from the solution. During the crystallization under magnetic field, there exists Lorentz force acting selectively on the charged molecules/ion, causing them to move in a cyclotron motion. In the interface of solution-crystals this motion could possibly increases the perturbation on the chemical potential, which may lead to the changes in the crystal structure.

In the perspective of the present work, the disorders induced by the field manifest themselves as the changes in the relative positions of the TCNQ molecules. The new relative positions in the 5 T crystals result in additional forces that prevent the system from entering the delocalization state with the same degree as the 0 T crystals in the high-pressure phase.

5. Conclusion

The results explained in the preceding sections demonstrate the changes in the electronic structure of the crystals grown under magnetic field, which are too microscopic to be detected by means of conventional methods. These microscopic changes, however, affect the electronic structure to change the properties of the crystals remarkably. Considering that the electron distribution along the TCNQ columns in the high-pressure phase of the 5 T crystals is different from that of the 0 T crystals, their transport properties in the high-pressure phase must be very interesting, and it will be explored in the incoming works.

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Figure caption

Figure 1. Absorption spectra in the C-CN stretching region at several pressures.

Figure 2. Pressure dependence of the frequency of the C-CN stretching in 0 T and 5 T crystals. The error bars represent the width of the absorption bands, and the vertical dotted lines in the graph indicate the transition points in respective crystals.

Figure 3. Pressure dependence of the integrated intensity of EMV mode observed at 1184 cm^{-1} at ambient pressure in 0T and 5 T crystals.

Figure 4. Pressure dependence of the frequency of EMV mode observed at in 0T and 5 T crystals.

Figure 5. Pressure dependence of the frequency of the C-H stretching in 0 T and 5 T crystals.

Figure 1.

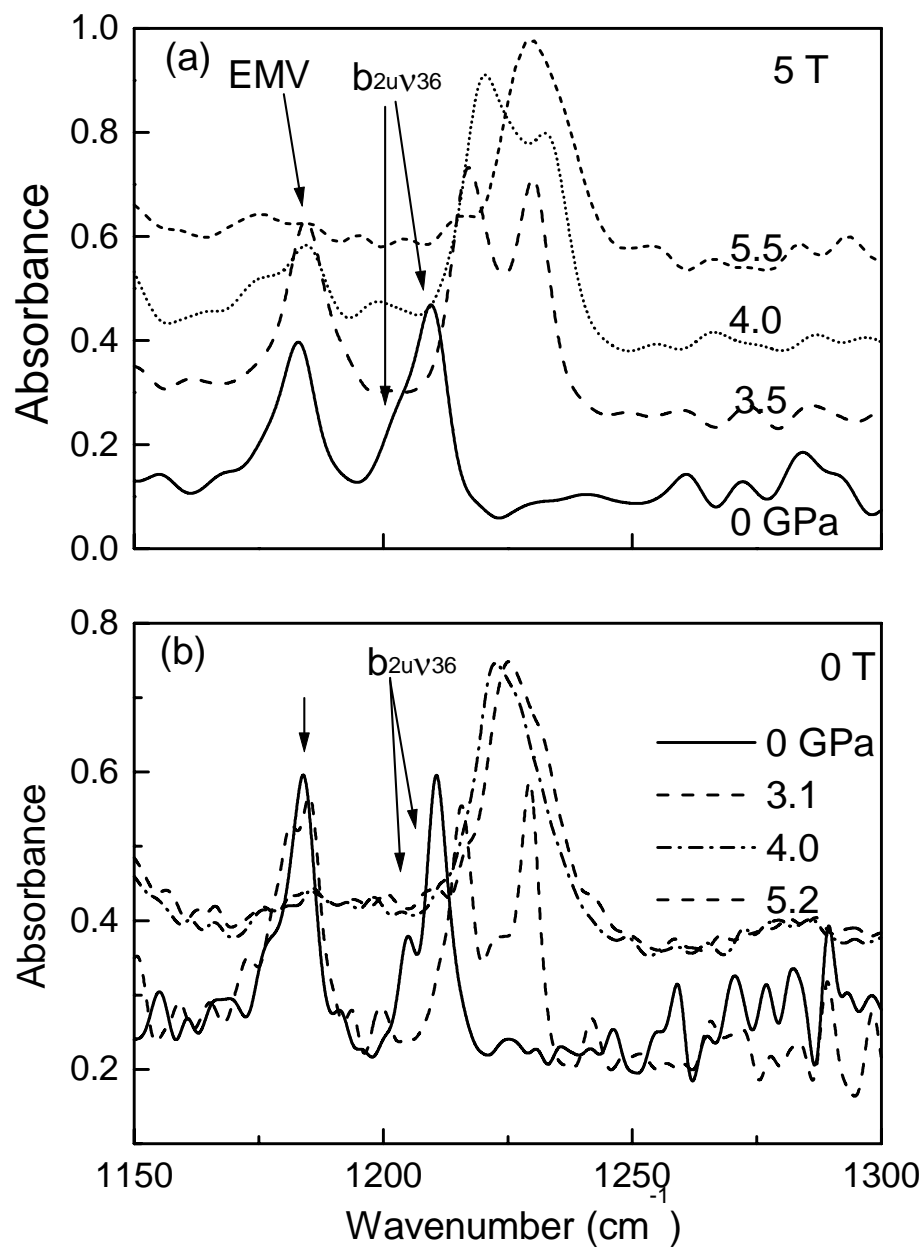


Figure 2.

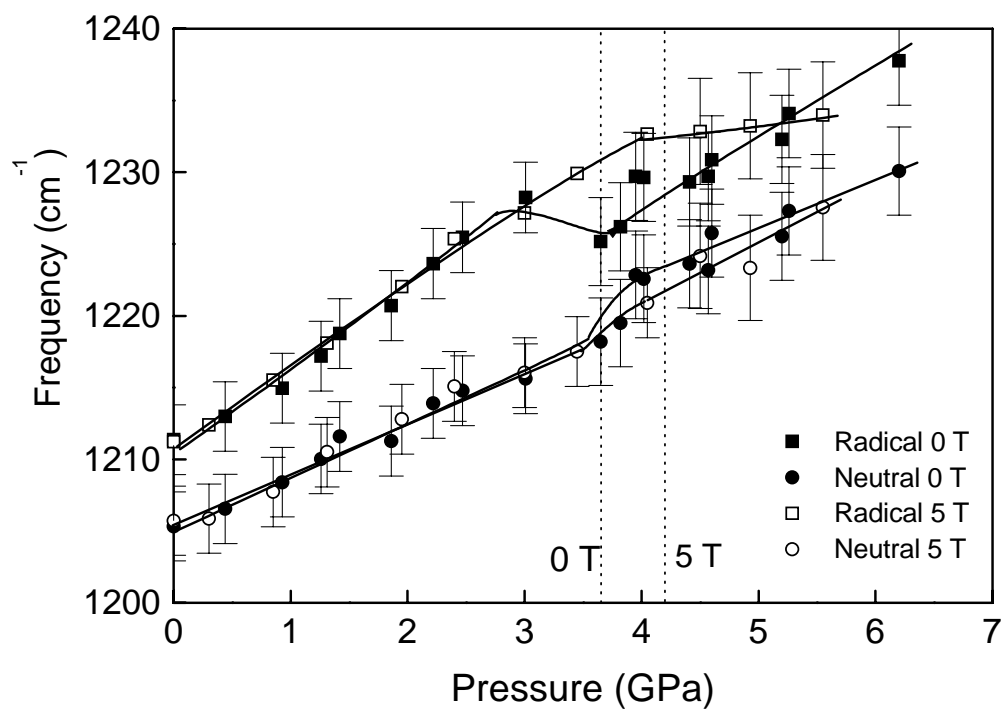


Figure 3.

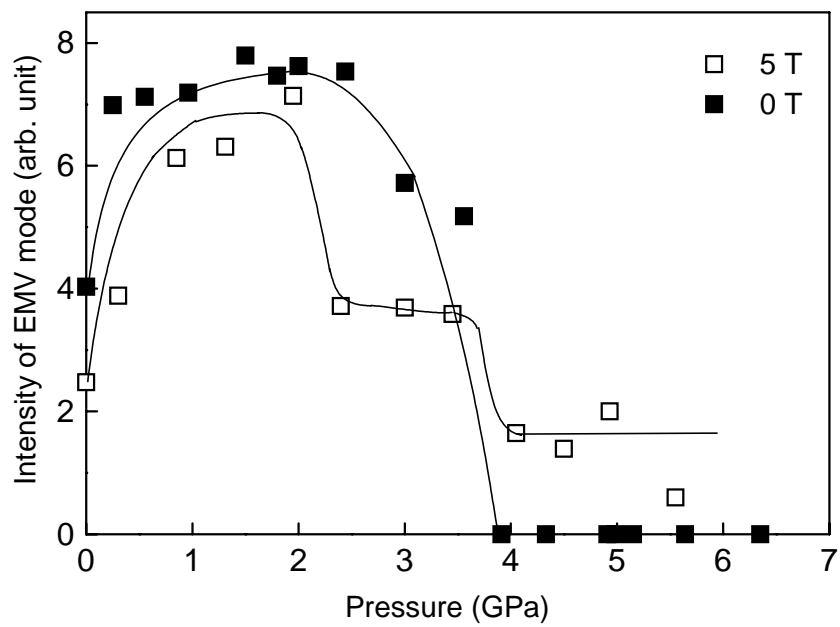


Figure 4.

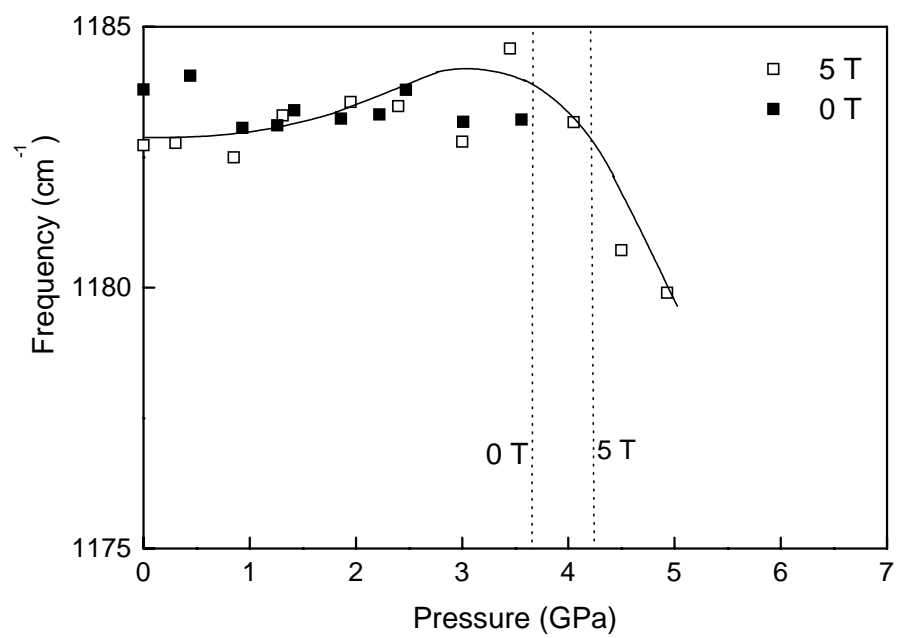


Figure 5

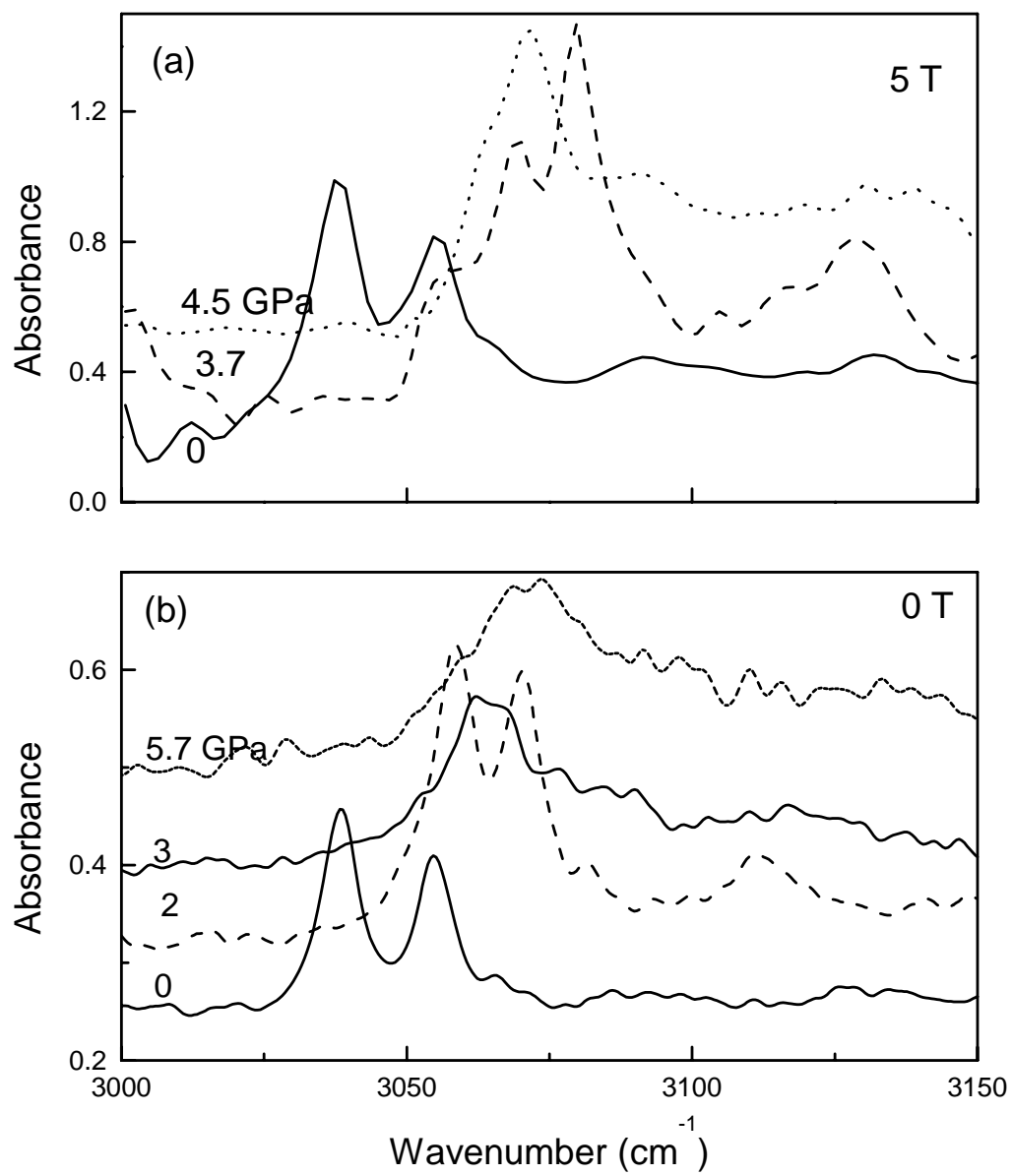


Figure 6.

